REMARKS

Entry of the above amendment and further examination and reconsideration of the subject application are respectfully requested. Claims 1-40 are pending in the application. Claims 18-40 have been withdrawn from consideration in response to a restriction requirement. Claims 1 and 9 have been rewritten to specify an aqueous dispersion or emulsion of a polymer or organic pigment instead of an aqueous mixture of a polymer or pigment. Support for these changes may be found generally throughout the application and, specifically, at paragraphs 12-15, and claims 8 and 24 as originally filed. Claims 5 and 8 have been canceled. Claim 7 has been amended to include a part of the subject matter of claim 8. Applicants include herewith a listing of the claims showing changes made by the current amendment.

Restriction Requirement

Applicants acknowledge the Examiner's statements regarding the election / restriction requirement.

Rejection of Claims 1-17 under 35 U.S.C. §112

The Office rejected claims 1-17 under 35 U.S.C. § 112, second paragraph, allegedly for being indefinite because the step of agitating does not include living cells. In addition, the Office alleges that the differences between

the polymer, pigment, and disruption agent are not clear because a polymer or pigment each could be large particles and, hence, a disruption agent. Although Applicants respectfully traverse the rejection and the statements made in support thereof, Applicants have amended Claim 1 and canceled claim 5 to advance the prosecution of the application. Amended claim 1 now refers to agitating an aqueous dispersion or emulsion of a polymer or organic pigment comprising living cells. Living cells, therefore, now are included explicitly in the step of agitating.

Rewritten claim 1 also clearly sets forth the differences between the polymer and pigment and the particulate disruption agent. The polymer or organic pigment cited in rewritten claim 1 is in the form of an aqueous dispersion or emulsion. Persons skilled in the art would recognize and understand that dispersed or emulsified polymer or organic pigment particles, because of their small size, among other things, would not function efficiently as particulate disruption agents and would not confuse the two. Applicants submit, therefore, that the differences between these components in amended claim 1 are both clear and definite. Applicants remind the Office that "[t]he primary purpose of this requirement of definiteness of claim language is to ensure that the scope of the claims is clear so the public is informed of the boundaries of what constitutes infringement of the patent." M.P.E.P. § 2173. One of ordinary skill in the art attempting to release ATP from living cells

present in an aqueous dispersion of a polymer or organic pigment and trying to determine whether such action infringes the instant claims would be able to make that determination easily.

The Office argues also that claims 5 and 10 encompass the use of identical materials for both "pigment" and "disrupting agent" which makes the differences between these components unclear. In response, Applicants have canceled claim 5 by the present amendment and rewritten claim 1 to specify an "organic pigment" instead of "pigment". Applicants submit that these changes further clarify the differences between these components.

In view of the amendment to the claims and for at least the reasons stated above, Applicants believe that the rejection under 35 U.S.C. § 112, second paragraph, has been overcome. Applicants respectfully request that the rejection be withdrawn.

Rejection of Claims 1-11 under 35 U.S.C. 102(b)

Claims 1-11 stand rejected under 35 U.S.C. 102(b) as allegedly being anticipated by German Patent Application DE 196 25 137 A1 to Balk et al. ("Balk"). For at least the reasons below, this rejection should be withdrawn.

Balk does not disclose or suggest each feature of rewritten claim 1. In particular, Balk does not disclose or suggest agitating an aqueous dispersion of

a polymer or pigment. Balk also does not disclose or suggest using a particulate disruption agent to disrupt living cells.

The Office argues that the dispersion of polystyrene disclosed on page 6 of Balk can be considered as a particulate disruption agent within the meaning of the claims. Applicants respectfully disagree and remind the Office that the pending claims must be given "their broadest reasonable construction in light of the specification as it would be interpreted by one of ordinary skill in the art." *In re Am. Acad. of Sci. Tech. Ctr.*, 367 F.3d 1359, 1364[, 70 USPQ2d 1827] (Fed. Cir. 2004). ...The broadest reasonable interpretation of the claims must also be consistent with the interpretation that those skilled in the art would reach. *In re Cortright*, 165 F.3d 1353, 1359, 49 USPQ2d 1464, 1468 (Fed. Cir. 1999)" MPEP §2111. If a skilled person looks at the disclosure of Balk on page 6 and Table 1, the skilled person would see that the styrene dispersion to which the Office refers is not used as a disruption agent but is simply one of several emulsions and dispersions tested by Balk for the presence of living cells. Balk, instead, only discloses chemical agents to disrupt (lyse) cells. Moreover, the skilled person on reading Applicants' specification (see, for example, paragraphs 23-27) and the disclosure of Geciova et al (cited by the Office) would not consider the styrene dispersion disclosed by Balk to be a particulate disruption agent. For example, polymer dispersions as disclosed by Balk typically have exceedingly small particles sizes (for example, 50-200 nm) in

comparison to particulate disruption agents (typically 0.1 - 1 mm or 100,000 - 1,000,000 nm, see Geciova, page 544). Applicants refer the Office to the excerpt from Odian, Principles of Polymerization (John Wiley & Sons, **1981**, page 325), included herewith, for a discussion of particle sizes of polymer dispersions. Persons skilled in the art would certainly understand that such small particle sizes make polymer dispersions ineffective for disruption of living cells because the individual particles have insufficient kinetic energy to disrupt cell walls. Applicants' disclosure also clearly indicates that the particulate disruption agent is in addition to the polymer dispersion, thus a separate and distinct component from the polymer dispersion *per se*. Further, an aqueous dispersion of polystyrene or any polymer is not properly considered as a plastic. Persons skilled in the art would certainly know and understand a plastic to be a high polymer that can be formed or molded under heat. An aqueous dispersion of polystyrene in neither a high polymer nor can be formed or molded. Applicants respectfully direct the Examiner's attention to the definitions of "plastic" and "dispersion" from Hawley's Condensed Chemical Dictionary (John Wiley & Sons, **2001**, pages 884 and 415) attached hereto, which clearly reflects well understood and well known terminology.

When analysed properly, the disclosure of Balk does not fairly disclose or suggest agitation of a aqueous dispersion of a polymer or organic pigment in the presence of a particulate disruption agent and, thus, does not anticpate the

claimed invention. Applicants, therefore, request that the rejection be withdrawn.

Rejection of Claims 1-3 under 35 U.S.C. 102(b)

Claims 1-3 stand rejected under 35 U.S.C. 102(b) as allegedly being anticipated by European Patent Application EP 0 542 790 B1 to Pahuski et al. ("Pahuski"). For at least the reasons below, this rejection should be withdrawn.

Pahuski fails to disclose or suggest each feature of rewritten claim 1. For example, Pahuski does not disclose or suggest agitating an aqueous dispersion or emulsion of a polymer or organic pigment. In addition, Pahuski fails to disclose or suggest agitation of an aqueous dispersion in the presence of a particulate disruption agent sufficient to cause rupturing of and release of ATP from living cells present in the dispersion.

The Office argues that the procedures disclosed in Pahuski anticipate the claimed invention because living cells are vortexed in the presence of polystyrene beads and Triton X-100, a detergent derived from poly(ethylene oxide). The Office asserts that Triton X-100 is a polymer and that polystyrene beads are used in Pahuski to cause disruption of the living cells.

Applicants note, however, that Triton X-100 is a water soluble polymer, assuming that it would legitimately be considered a polymer by persons skilled in the art. As a water-soluble polymer, it cannot also be an aqueous dispersion

because, by definition, a dispersion must consist of at least 2 phases. Pahuski, therefore, fails to disclose the step of agitating an aqueous dispersion or emulsion of a polymer or organic pigment.

Pahuski also fails to disclose disruption of living cells by agitation in the presence of a particulate disruption agent. Pahuski discloses that lysing of the microbial cells is accomplished chemically and occurs separately from the step of agitating of the cell samples with polyestyrene beads (see, for example, page 7, lines 18-2; Reference Example 2, page 9, lines 36-37; and Example 3, lines 41). The polystyrene beads, instead, are disclosed by Pahuski as a microparticulate carrier for the collection of cells during the centrifugation steps of the cell process and not as an agent for the disruption of cell walls (see Pahuski, page 6, lines 56 – page 7, line 1). Pahuski, in fact, discloses that the microparticulate carrier "must be inert to the testing and evaluation that will be performed on the cell pellet" and "should be invisible in cell staining techniques if a microscopic examination is to be performed..." (Pahuski, page 7, lines 7-9). These statements are inconsistent with the Office's assertion that the polystyrene beads in Pahuski are functioning as a disruption agent as there would be no intact cells present for testing, evaluation, or for staining if the polystyrene beads were disrupting cell membranes. In addition, the skilled person would not consider the polystyrene beads disclosed in Pahuski to be a disruption agent because of their small size (0.25- 2.5 μm or 0.00025 – 0.0025

mm). As noted above, this size is well below the typical range of 0.1- 1.0 mm) that is recognized in the art as useful for particulate disruption agents (see Geciova, page 544).

For at least the reasons set forth above, Pahuski does not anticipate the invention as claimed. Applicants respectfully request that the rejection be withdrawn.

Rejection of Claims 1-6 under 35 U.S.C. §102(b)

Claims 1-6 stand rejected under 35 U.S.C. 102(b) as allegedly being anticipated by Calvo-Bado et al. *Applied and Environmental Microbiology*, April 2003, Vol. 69, p. 2116-2125 ("Calvo-Bado"). For at least the reasons below, this rejection should be withdrawn.

Calvo-Bado does not disclose or suggest agitating an aqueous dispersion or emulsion of a polymer or organic pigment in the presence of a particulate disruption agent. Thus, Calvo-Bado fails to disclose or suggest each feature of rewritten claim 1 and cannot anticipate the claimed invention.

The Office argues that Calvo-Bado discloses agitating an aqueous mixture of filtration sand containing living cells from horticultural irrigation water in the presence of a particulate disruption agent. The Office argues that the filtration sand is a "pigment" within the meaning of the instant claims. The Office also argues that the sand samples disclosed by Calvo-Bado are

reasonably expected to contain at least some amounts of plant residues or cellulosic polymers.

Although Applicants respectfully disagree with the Office, Applicants believe that rejection is overcome in view of the amended claims. Assuming that persons skilled in the art would consider the filtration sand disclosed in Calvo-Bado as a "pigment", this sand would not be considered as an organic pigment as recited in the amended claims. The Office further argues that the sand samples are reasonably expected to contain at least some amounts of plant residues or cellulosic polymers. Applicants, however, are unable to find any explicit or implicit disclosure of plant residues or cellulosic polymers in the disclosure of Calvo-Bado and, therefore, assume that the Office is asserting that these materials would be inherently present in the sand samples. The Office is respectfully reminded that "To establish inherency, the extrinsic evidence 'must make clear that the missing descriptive matter *is necessarily present* in the thing described in the reference. . . The mere fact that a certain thing may result from a given set of circumstances *is not sufficient*.'" M.P.E.P. § 2112.IV (internal citations omitted, emphasis added). Inherency, however, may not be established by probabilities or possibilities." *Id.* (internal citations omitted). The Office, however, has not met its burden of "providing a basis in fact and/or technical reasoning" to show that the plant residues or cellulosic polymers necessarily are present in the sand samples of Calvo-Bado. Moreover,

assuming that the sand samples do contain plant residues or cellulosic polymers, there is no teaching or suggestion that these materials are present as a aqueous dispersion or emulsion. The disclosure of Calvo-Bado, therefore, does not teach or suggest an aqueous dispersion or emulsion of a polymer or organic pigment as recited in claim 1. Accordingly, Calvo-Bado does not anticipate the claimed invention, and the rejection should be withdrawn.

Rejection of Claims 1-17 under 35 U.S.C. §103(a)

Claims 1-17 stand rejected under 35 U.S.C. §103(a) as being unpatentable over European Patent Application, EP 0 542 790 B1 to Pahuski et al. ("Pahuski"); Calvo-Bado et al. *Applied and Environmental Microbiology*, April 2003, Vol. 69, p. 2116-2125 ("Calvo-Bado"); and German Patent Application DE 196 25 137 A1 to Balk et al. ("Balk") taken with Geciova et al, "Methods for disruption of microbial cells for potential use in the dairy industry - a review," *International Dairy Journal*, Vol. 12 (2002), p. 541-553; and US Patent No. 5,017,564 to Makino et al ("Makino"). For at least the following reasons, this rejection should be withdrawn.

The Office argues that Balk, Pahuski, and Calvo-Bado teach and suggest all the structural elements for disrupting living cells with beads in polymer/pigment dispersions for the release of ATP (Office Action at 8). Applicants respectfully submit that the Office has mischaracterized the

disclosures of Pahuski, Balk, and Calvo-Bado and has not provided a reason why a person of ordinary skill in the art would modify the cited references to make the claimed invention. The deficiencies of Pahuski, Calvo-Bado, and Balk have been discussed above and are incorporated herein by reference. As Applicants have noted, Pahuski, Calvo-Bado, and Balk, either individually or in any reasonable combination, do not fairly teach or suggest agitating an aqueous dispersion or emulsion of a polymer or organic pigment in the presence of a particulate disruption agent sufficient to cause rupturing of and release of ATP from living cells. For example, Balk explicitly discloses chemical lysis of living cells as a reliable means to detect ATP and is absolutely silent on alternative cell disruption methods. Similarly, Pahuski discloses only chemical disruption methods and does not address disruption of living cells within dispersions or emulsions of polymers or pigments. Calvo-Bado discloses glass beads as a disruption agent but makes no suggestion of their application to dispersions or emulsions of polymers or pigments. Moreover, none of these references, either individually or in any reasonable combination, would have provided a reason or motivation that would have prompted the skilled person to use a particulate disruption agent with a dispersion or emulsion of a polymer or pigment to make the claimed invention.

The disclosure of Geciova does not remedy the deficiencies of Balk, Pahuski, and Calvo-Bado. The Office argues that "one of skill in the art would

have been motivated to modify bead size and agitation speed with regard to the type of living cells as adequately taught and/or suggested by Geciova et al." Applicants respectfully disagree and note that this argument incorrectly assumes that the cited art provides a motivation to use a bead mill in the first place. The disclosure of Geciova teaches a wide variety of both chemical, mechanical, enzymatic, and physical disruption methods but provides no disclosure that would cause the person of ordinary skill to select particulate disruption agents in combination with aqueous dispersions or emulsions of polymers or organic pigments. Geciova is absolutely silent on dispersions of polymers or pigments, teaches generally all of the above methods with no particular emphasis on any single method, and thus provides no guidance to select one particular method over the others.

Makino does not cure the deficiencies of Balk, Pahuski, Calvo-Bado, or Geciova. In fact, Applicants respectfully submit that Makino has no meaningful relationship at all to the other cited references or to the claimed invention. The Office argues that "one would have been motivated to use polymers and/or colorants to stabilize ATP released from the disrupted living cells as adequately taught and/or suggested by US 5,017,564 for the expected benefits in stabilizing ATP for consecutive measurement and maximizing ATP amount correlation with the quantify of cells present in the analyzed samples." Applicants interpret this argument to mean that a person of skill in the art

would intentionally add polymers or colorants to an ATP assay to prevent the ATP from decomposing before it can be detected, and thereby arrive at the claimed invention.

Applicants respectfully traverse this argument for at least 3 reasons. First, the divergent nature of Makino and the other cited art does not suggest their combination. The disclosure of Makino has nothing to do with release or detection of ATP from living cells. Instead, Makino is drawn to increasing the stability and, hence, the shelf life the disodium salt of ATP within a solid, pharmaceutical composition for ingestion by humans. On the other hand, Balk, Pahuski, Calvo-Bado, and Geciova are drawn to detecting living cells within various aqueous environments by disruption of the cells and detection of the ATP released. The Office has not explained why the person of ordinary skill in the art would combine the divergent teachings of these references.

Second, the Office has not provided an explanation of why a skilled person would expect a method for stabilizing the disodium salt of ATP against high heat and humidity in the solid phase would be relevant or applicable to stabilization of ATP in aqueous media under conditions. There is no disclosure in the cited art that would suggest that the method of Makino, which is directed to a different form of ATP, different conditions, and different form of materials, would be useful in the ATP assays disclosed in Balk, Pahuski, and Calvo-Bado.

Third, the Office has not provided any line of reasoning or explanation to suggest the desirability of "stabilizing" ATP for purposes of detecting living cells. Based on the cited art, it would be entirely reasonable for the skilled person to expect that such stabilization would interfere with the analysis and detection of ATP because such analyses depend on the reaction of ATP with another reagent such as, for example, luceriferase.

For at least the above reasons, Applicants respectfully submit that the Office fails to make a *prima facie* case of obviousness. First, as set forth above, none of the cited references, either individually or in any reasonable combination, would have taught all of the limitations of the presently claimed invention. In particular, the cited art would not have taught or suggested agitating an aqueous dispersion or emulsion of a polymer or organic pigment, comprising living cells, in the presence of a particulate disruption agent sufficient to cause disruption of the cells and release of the ATP.

Second, the Office does not provide an proper reason or motivation to combine the cited art in the allegedly obvious manner. The Office has provided no rational connection between that which is taught in the cited references and the limitations of the presently claimed invention. The motivations stated by the Office are broad, not supported by the cited art, and would not have motivated a person skilled in the art at the time the invention was made to look to particular sources of information, to select particular elements, and to combine

them to obtain Applicants' claimed process. Finally, the cited references necessarily would not have provided a reasonable expectation of success since they lack any suggestion or teaching of the limitations of Applicants' process.

Nevertheless, even if one assumes a proper motivation to combine the cited art, the unpredictable nature of the cell disruption techniques for the detection of living cells in aqueous dispersions of polymers weighs heavily in favor of patentability. Specifically, Applicants experimental results in Table 2, page 23, of the instant specification show that simply substituting one cell disruption method for another does not yield predictable results. This unpredictability applies to both chemical and mechanical lysing methods. By contrast, use of a particulate disruption agent, i.e., glass beads, dramatically and unexpectedly increases the release of ATP. It is the Applicants' respectful submission, therefore, that there can be no finding of obviousness by the Office and that the rejection is in error. Applicants request that the rejection be withdrawn.

In summary, for at least the reasons set forth above, the references relied upon and arguments set forth by the Office do not support rejection of the claims under §102(b) or §103(a). Accordingly, Applicants earnestly request reconsideration of the application and withdrawal of all rejections.

Respectfully submitted,

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Hawley's

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Fourteenth Edition

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disodium orthophosphate. See sodium phosphate, dibasic.

disodiumphenyl phosphate. $C_6H_5Na_2PO_4$.
Properties: White powder. Soluble in water; insoluble in acetone and ether.
Use: Reagent for milk pasteurization.

disodium phosphate. See sodium phosphate, dibasic.

disodium pyrophosphate. See sodium pyrophosphate, acid.

disodium tartrate. See sodium tartrate.

disperse dye. See dye, disperse.

disperse phase. See phase (2); colloid chemistry.

dispersing agent. A surface-active agent added to a suspending medium to promote uniform and maximum separation of extremely fine solid particles, often of colloidal size. True dispersing agents are polymeric electrolytes (condensed sodium silicates, polyphosphates, lignin derivatives); in nonaqueous media sterols, lecithin and fatty acids are effective.
Use: Wet-grinding of pigments and sulfur; preparation of ceramic glazes, oil-well drilling muds, insecticidal mixtures, carbon black in rubber, and water-insoluble dyes.
See emulsion; detergent.

dispersion. (1) A two-phase system where one phase consists of finely divided particles (often in the colloidal size range) distributed throughout a bulk substance, the particles being the disperse or internal phase, and the bulk substance the continuous or external phase. Under natural conditions, the distribution is seldom uniform; but under controlled conditions, the uniformity can be increased by addition of wetting or dispersing agents (surfactants) such as a fatty acid. The various possible systems are: gas-liquid (foam), solid-gas (aerosol), gas-solid (foamed plastic), liquid-gas (fog), liquid-liquid (emulsions), solid-liquid (paint), and solid-solid (carbon black in rubber). Some types, such as milk and rubber latex, are stabilized by a protective colloid that prevents agglomeration of the dispersed particles by an abherent coating. Solid-in-liquid colloidal dispersions (loosely called solutions) can be precipitated by adding electrolytes that neutralize the electrical charges on the particles. Larger particles will gradually coalesce and either rise to the top or settle out. [illegible]

important property of optical glass.
See refraction.

"Dispersite" *[Uniroyal].* TM for water dispersions of natural, synthetic, and reclaimed rubbers and resins.
Use: Adhesives for textiles, paper, shoes, leather, tapes; coatings for metal, paper, fabrics, carpets; protective (strippable) for saturating paper, felt, book covers, tape, jute pads; for dipping tire cords. Can be applied by spraying, spreading, impregnation, saturation.

"Disperson" *[Crompton & Knowles].* TM for wettable grades of zinc, calcium, and other metallic stearates.
Use: Where easy dispersion in water is desired.

"Disperson OS" *[ICI].* TM for an oil-soluble emulsifying agent composed of an 8% solution of a polyethenoxy compound in isopropanol. Designed especially for dispersion of oil spills in seawater. Claimed to be biodegradable and to have low toxicity for fish and other marine organisms. Amount needed said to be from 20 to 25% of the oil volume.

displacement. Chemical change in which one element enters a compound in place of another, the latter being set free.

displacement series. See activity series.

disposal, waste. See waste control; chemical waste; radioactive waste.

disproportionation. A chemical reaction in which a single compound serves as both oxidizing and reducing agent and is thereby converted into a more oxidized and a more reduced derivative. Thus, a hypochlorite upon appropriate heating yields a chlorate and a chloride, and an ethyl radical formed as an intermediate is converted into ethane and ethylene.
See transalkylation.

dissociation. The process by which a chemical combination breaks up into simpler constituents as a result of either (1) added energy, as in the case of gaseous molecules dissociated by heat, or (2) the effect of a solvent on a dissolved polar compound (electrolytic dissociation), e.g., water on hydrogen chloride. It may occur in the gaseous, solid, or liquid state, or in solution. All electrolytes dissociate to a greater or less extent in polar solvents. The degree of dissociation can be used to determine the equilibri-

etc.), (11) expansion possibilities.

"Plas-Chek" *[Ferro].* TM for plasticizers.

"Plasdone" *[International Specialty].* TM for the pharmaceutical grade of polyvinylpyrrolidone.
Use: Tablet binding and coating agent, detoxicant and demulcent lubricant in ophthalmic preparations, film-forming agent in medical aerosols.

plasma. (1) The portion of the blood remaining after removal of the white and red cells and the platelets; it differs from serum in that it contains fibrinogen, which induces clotting by conversion into fibrin by activity of the enzyme thrombin. Plasma is made up of more than 40 proteins and also contains acids, lipids, and metal ions. It is an amber, opalescent solution in which the proteins are in colloidal suspension and the solutes (electrolytes and nonelectrolytes) are either emulsified or in true solution. The proteins can be separated from each other and from the other solutes by ultrafiltration, ultracentrifugation, electrophoresis, and immunochemical techniques.
(2) Two kinds of plasma are recognized by physicists, namely, a particle plasma and a reactor plasma. A particle plasma is a neutral mixture of positively and negatively charged particles interacting with an electromagnetic field, which dominates their motion. Temperatures of 10,000 to 15,000C can be reached. Such plasma, formed by sudden energy releases can be utilized as an energy source, as in magnetohydrodynamics. Reactor plasmas, on the other hand, are composed of positively charged ions of hydrogen isotopes (deuterium, tritium); the electric charge is the controlling factor. These are used in nuclear fusion devices, where temperatures of 74,000,000C have been attained and still higher temperatures are expected. These plasmas also respond to electromagnetic forces that are used to confine them. See magnetohydrodynamics; fusion; tokamak.

plasma volume expander. A substance used to partially or wholly replace blood plasma in treatment of the injured. Most important are gelatin, polyvinylpyrrolidone, and dextran.

plasmid. A strand or fragment of genetic material existing outside the chromosomes in certain types of bacteria. R-type plasmids, which are present in *E. coli*, impart resistance to antibiotics in organisms that are exposed to them. The plasmids can be transferred from animals to humans, as well as to other, harmful bacteria that also become resistant to antibiotics. Feeding of traces of antibiotics to animals is believed to promote the growth of *E. coli* and, thus, to produce strains of pathogenic bacteria that are not

cycline, and chlortetracycline. Synthetic plasmids have been used successfully in recombinant DNA research.

plasmin. See fibrinolysin.

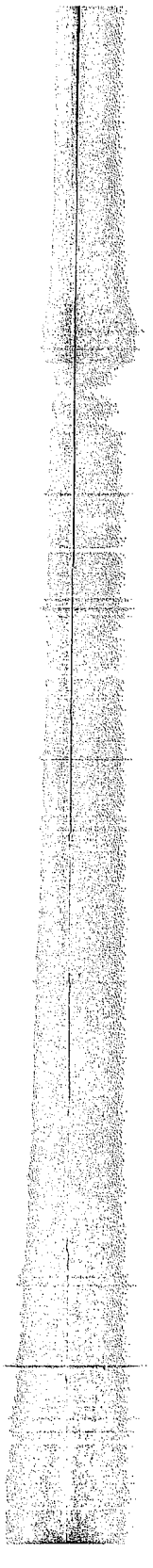
plasmoquin. (pamaquine; plasmochin; 8-dimethylamino-isoamyl-6-methoxyquinoline). $C_{19}H_{28}N_2O$.
Properties: Yellow powder. Mw 300.2. Insoluble in water.
Use: Antimalarial.

"Plastacele" *[Du Pont].* TM for cellulose acetate flake, a fine white powder used for molding powders, films, sheets, rods, and tubes.

plaster of Paris. See calcium sulfate.

"Plasthall" *[Hall].* TM for a broad range of monomeric and polymeric plasticizers used in polymers and elastomers. Types include adipates, glutarates, trimellitates, azelates, sebacates, and tallates.

plastic. (1) Capable of being shaped or molded with or without the application of heat. Soft waxes and moist clay are good examples of this property. See plasticity. (2) A high polymer, usually synthetic, combined with other ingredients, such as curatives, fillers, reinforcing agents, colorants, plasticizers, etc.; the mixture can be formed or molded under heat and pressure in its raw state and machined to high dimensional accuracy, trimmed, and finished in its hardened state. The thermoplastic type can be resoftened to its original condition by heat; the thermosetting type cannot.
Plastics in general (including all forms) are sensitive to high temperatures, among the more resistant being fluorocarbon resins, nylon, phenolics, polyimides, and silicones, though even these soften or melt above 260C. Other types (cellulosics, polyethylene, acrylic polymers, polystyrene) are combustible when exposed to flame for a short time and still others (polyurethane) burn with evolution of toxic fumes.
Engineering plastics are those to which standard metal engineering equations can be applied; they are capable of sustaining high loads and stresses and are machinable and dimensionally stable. They are used in construction, as machine parts, automobile components, etc. Among the more important are nylon, acetals, polycarbonates, ABS resins, PPO/styrene, and polybutylene terephthalate.
Fibers, films, and bristles are examples of extruded forms. Plastics may be shaped by either compression molding (direct pressure on solid material in a hydraulic press) or injection molding (injection of a measured amount of material into a mold in liquid form). The latter process is most generally used, and



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articles of considerable size can be produced. Because of their dielectric properties, plastics are essential components of electrical and electronic equipment (especially for use within the human body).

Plastics can be made into flexible and rigid foams by use of a blowing agent; these foams are light and strong, and the rigid type is machinable. They are collectively called cellular plastics. Plastics can also be reinforced, usually with glass or metallic fibers, for added strength. They are laminated to paper, cloth, wood, etc. for many uses in the packaging, electrical, and furniture industries; they also can be metal-plated. Plastic pipe is widely used for underground transportation of gases and liquids over long distances and intraplant.

Several natural materials (waxes, clays, and asphalts) have rheological properties similar to synthetic products, but because they are not polymeric, are not considered true plastics. Certain proteins (casein, zein) are natural high polymers from which plastics are made (buttons and other small items), but they are of decreasing importance.

Plastics have permeated industrial technology. Not only have they replaced and improved upon many materials formerly used, but they also have made possible industrial and medical applications that would have been impracticable with older technologies. Their major application areas are (1) automobile bodies and components, boat hulls; (2) building and construction (siding, piping insulation, flooring); (3) packaging (vapor-proof barriers, display cartons, bottles, drum linings); (4) textiles (carpets, cordage, suiting, hosiery, drip-dry fabrics, etc.); (5) organic coatings (paint and varnish vehicles); (6) adhesives (plywood, reinforced plastics, laminated structures); (7) pipelines; (8) electrical and electronic components; (9) surgical implants; (10) miscellaneous (luggage, toys, tableware, brushes, furniture, etc.). The Nobel prize was awarded in 2000 for work on developing conducting plastics. For additional information refer to The Society of the Plastics Industry. See polymer, high; cellular plastic; reinforced plastic; foam, plastic; plastic pipe. See Appendix III for a history of the industry.

plastic film. A thermoplastic film less than 0.022 cm (0.010 inch) in thickness.

plastic flow. A type of rheological behavior in which a given material shows no deformation until the applied stress reaches a critical value called the yield value. Most of the so-called plastics do not exhibit plastic flow. Common putty is an example of a material having plastic flow.

plastic foam. See foam, plastic; cellular

retain the shape so induced, either permanently or for a definite time interval. It may be considered the reverse of elasticity. Application of heat and/or special additives is usually required for optimum results.

See thermoplastic; plasticizer.

plasticizer. An organic compound added to a high polymer both to facilitate processing and to increase the flexibility and toughness of the final product by internal modification (solvation) of the polymer molecule. The latter is held together by secondary valence bonds; the plasticizer replaces some of these with plasticizer-to-polymer bonds, thus aiding movement of the polymer chain segments. Plasticizers are classed as primary (high compatibility) and secondary (limited compatibility). Polyvinyl chloride and cellulose esters are the largest consumers of plasticizers; they are also used in rubber processing. Among the more important plasticizers are nonvolatile organic liquids and low-melting solids (e.g., phthalate, adipate, and sebacate esters), polyols such as ethylene glycol and its derivatives, tricresyl phosphate, castor oil, etc. Camphor was used in the original modification of nitrocellulose to "Celluloid."

See plastisol; softener.

plastic pipe. Tubes, cylinders, conduits, and continuous length piping made (1) from thermoplastic polymers unreinforced (polyethylene, polyvinyl chloride, ABS polymers, polypropylene) or (2) from thermosetting polymers (polyesters, phenolics, epoxies) blended with 60–80% of such reinforcing materials as chopped asbestos or glass fibers to increase strength. The latter type is a reinforced plastic. In general the properties of plastic tubing or pipe are those of the polymers that comprise it. Most have good resistance to chemicals, corrosion, weathering, etc., combined with flexibility, light weight, and high strength. They are combustible but generally slow burning. The reinforced type is widely used as underground conduit for transportation of gases and fluids, including city water services, sewage disposal systems, etc. Its use in buildings is subject to local building codes.

plastic, reinforced. See reinforced plastic.

plastisol. A dispersion of finely divided resin in a plasticizer. A typical composition is 100 parts resin and 50 parts plasticizer, forming a paste that gels when heated to 150C as a result of solvation of the resin particles by the plasticizer. If a volatile solvent is included, the plastisol is called an organosol. Plastisols are used for molding thermoplastic resins, chiefly polyvinyl chloride.

Principles of — Polymerization —

SECOND EDITION

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cal Chain Polymerization

$k_p(fk_d[\mathrm{I}]/k_t)^{1/2}$ shows
and initiator concentra-

action Time (min)	Conversion (%)
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600	40
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-4-

Emulsion Polymerization

Emulsion polymerization refers to a unique process employed for some radical chain polymerizations. It involves the polymerization of monomers that are in the form of emulsions. The process is not similar to the previously described suspension polymerization (Sec. 3-13a-3) but is quite different in its mechanism and reaction characteristics. Emulsion polymerization differs from suspension polymerization in the type and smaller size of the particles in which polymerization occurs and in the kind of initiator employed. Emulsion polymerization involves a colloidal dispersion.

4-1 DESCRIPTION OF PROCESS

4-1a Utility

Emulsion polymerization was first employed on a large-scale in the United States for the production of synthetic styrene-butadiene rubber during the 1940s when the supplies of natural rubber were cut off during World War II. Emulsion polymerization is presently the predominant process for the commercial polymerizations of vinyl acetate, chloroprene, various acrylates, and copolymerizations of butadiene with styrene and acrylonitrile. Although not the predominant process, it is also used for methyl methacrylate, vinyl chloride, vinylidene chloride, and styrene. The final product of an emulsion polymerization, referred to as *latex*, is often used directly as an emulsion without prior separation of the polymer from water and the other components.

The emulsion polymerization process has several distinct advantages. The physical state of the emulsion (colloidal) system makes it easy to control the process. Thermal and viscosity problems are much less significant than in bulk polymerization. The products of emulsion polymerizations can in some instances be employed directly without further separations but with appropriate blending operations. Such applications involve coatings, finishes, floor polishes, and paints. Aside from the physical difference between the emulsion and other polymerization processes, there is one very significant kinetic difference. For the other processes there is an inverse relationship (Eq. 3-107) between the polymerization rate and the polymer molecular weight. This drastically limits one's practical ability to make large changes in the molecular weight of a polymer; for example, from 200,000 to 2,000,000 or

from 200,000 to 20,000. Large decreases in the molecular weight of a polymer can be made without altering the polymerization rate by using chain transfer agents. However, large increases in molecular weight can only be made by decreasing the polymerization rate by lowering the initiator concentration or lowering the reaction temperature. Emulsion polymerization is a unique process in that it affords a means of increasing the polymer molecular weight without decreasing the polymerization rate. Because of a different reaction mechanism emulsion polymerization has the advantage of being able to simultaneously attain both high molecular weights and high reaction rates.

4-1b Qualitative Picture

4-1b-1 Components and Their Locations

The physical picture of emulsion polymerization is based originally on the qualitative picture of Harkins [1] and the quantitative treatment of Smith and Ewart [2, 3] with recent contributions by Ugelstad and Hansen [4], Gardon [5,6], Gilbert and Napper [7,8] and others [9,10]. Table 4-1 shows a typical recipe for an emulsion polymerization [11]. This formulation was one of the early ones employed for the production of *GR-S* rubber but is typical of all emulsion polymerization systems. The main components are the monomer(s), *dispersant*, *emulsifier*, and water-soluble initiator. The dispersant is the liquid, usually water, in which the various components are dispersed in an emulsion state by means of the emulsifier. The ratio of water to monomer(s) is generally in the range 70/30 to 40/60 (by weight). The action of the emulsifier (also referred to as *surfactant* or *soap*) is due to its molecules having both hydrophilic and hydrophobic segments. Various other components may also be present in the emulsion system. Thus, a mercaptan is used in the above formulation as a chain transfer agent to control the polymer molecular weight. The initiator is the hydroperoxide–ferrous ion redox system and the function of fructose is probably to regenerate ferrous ion by reducing the ferric ion pro-

Table 4-1 Composition of a GR-S Recipe for Emulsion Polymerization of Styrene-Butadiene[a]

Component	Parts by Weight
Styrene	25
Butadiene	75
Water	180
Emulsifier (Dresinate 731)	5
n-Dodecyl mercaptan	0.5
NaOH	0.061
Cumene hydroperoxide	0.17
$FeSO_4$	0.017
$Na_4P_2O_7 \cdot 10\ H_2O$	1.5
Fructose	0.5

[a] Data from [11].

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duced in the initiation reaction (Eq. 3-36c). The sodium pyrophosphate acts to solubilize the iron salts in the strongly alkaline reaction medium. The emulsion system is usually kept in a well-agitated state during reaction.

The locations of the various components in an emulsion system will now be considered. When the concentration of a surfactant exceeds its *critical micelle concentration* (*CMC*), the excess surfactant molecules aggregate together to form small colloidal clusters referred to as *micelles*. The transformation of a solution to the colloidal state as the surfactant concentration exceeds the CMC occurs to minimize the free energy of solution (heat is liberated) and is accompanied by a sharp drop in the surface tension of the solution. Since the surfactant concentrations in most emulsion polymerizations (about 2–3%) exceed CMC by 1–3 orders of magnitude, the bulk of the surfactant is in the micelles. The shape of the micelles depends on the surfactant concentration. At lower surfactant concentrations (1–2%) the micelles are smaller and spherical (20–100 Å), each micelle containing about 50–150 surfactant molecules and one half that number of monomer molecules. At the higher surfactant concentrations, micelles are larger and rodlike in shape. Such micelles are 1000–3000 Å long with diameters approximately twice the length of an emulsifier molecule. The surfactant molecules are arranged in a micelle with their hydrocarbon ends pointed toward the interior of the micelle and their ionic ends outward toward the water. The number of micelles and their size depends on the amount of emulsifier used compared to the amount of monomer. Larger amounts of emulsifier yield larger numbers of smaller sized particles, that is, the surface area of the micelles increases with the amount of emulsifier.

When a water-insoluble or only slightly water-soluble monomer is added, a very small fraction dissolves and goes into solution. The water solubilities of the common monomers are quite low, although the spread is large, for example, styrene, butadiene, vinyl chloride, methyl methacrylate and vinyl acetate are soluble to the extent of 0.07, 0.8, 7, 16, and 25 g/liter at room temperature [5]. A larger but still small portion of the monomer enters the interior hydrocarbon part of the micelles. This is evidenced by X-ray and light scattering measurements which show that the micelles increase in size as the monomer is added [13]. The largest portion of the monomer is dispersed as *monomer droplets* whose size depends on the intensity of agitation. The droplets are probably stabilized by emulsifier molecules adsorbed on their surfaces. The diameter of the monomer droplets is usually not less than 1 μm (10,000 Å). Thus in a typical emulsion polymerization system, the monomer droplets are quite a bit larger than the monomer-containing micelles. Consequently, while the concentration of micelles is typically 10^{17}–10^{18} per milliliter, there are at most 10^{10}–10^{11} monomer droplets per milliliter. A further difference between micelles and monomer droplets is that the micelles have a much greater total surface area. The size, shape, and concentration of each of the various types of particles in the emulsion system are obtained from electron microscopy, light scattering, ultracentrifugation, photon correlation spectroscopy, and other methods [5,13].

4-1b-2 Site of Polymerization

The initiator is present in the water phase and this is where the initiating radicals are produced. The rate of radical production R_i is typically of the order of 10^{13}

radicals per milliliter per second. (The symbol ρ is often used instead of R_i in emulsion polymerization terminology.) The locus of polymerization is now of prime concern. The site of polymerization is not the monomer droplets since the initiators employed are insoluble in the organic monomer. Such initiators are referred to as oil-insoluble initiators. This situation distinguishes emulsion polymerization from suspension polymerization. Oil-soluble initiators are used in suspension polymerization and reaction occurs in the monomer droplets. The absence of polymerization in the monomer droplets in emulsion polymerization has been experimentally verified. If one halts an emulsion polymerization at an appropriate point before complete conversion is achieved, the monomer droplets can be separated and analyzed. An insignificant amount (approximately $< 0.1\%$) of polymer is found in the monomer droplets in such experiments. Polymerization of the monomer in solution undoubtedly takes place but does not contribute significantly, since the monomer concentration is low and propagating radicals would precipitate out of aqueous solution at very small (*oligomeric*) size.

Polymerization takes place almost exclusively in the interior of the micelles. The micelles act as a meeting place for the organic (oil-soluble) monomer and the water-soluble initiator. The micelles are also favored as the reaction site because of their high monomer concentration (similar to bulk monomer concentration) compared to the monomer in solution and their high surface-to-volume ratio compared to the monomer droplets. As polymerization proceeds, the micelles grow by the addition of monomer from the aqueous solution whose concentration is replenished by dissolution of monomer from the monomer droplets. A simplified schematic representation of an emulsion polymerization system is shown in Fig. 4-1. The system consists of three types of particles: monomer droplets, inactive micelles in which polymerization is not occurring, and active micelles in which polymerization is occurring. The latter are no longer considered as micelles but are referred to as *polymer particles*. An emulsifier molecule is shown as o– to indicate one end (o) is polar or ionic and the other end (–) nonpolar.

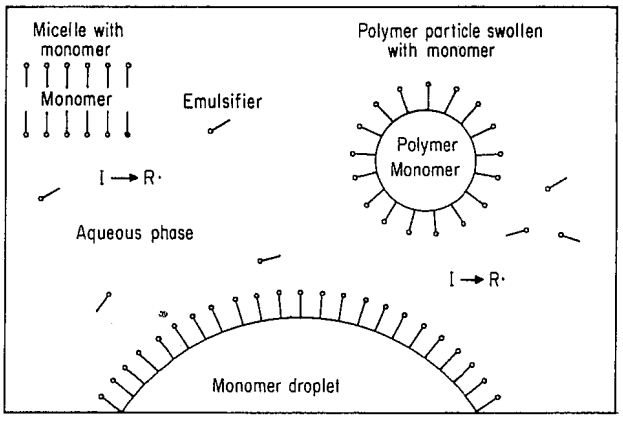

Fig. 4-1 Simplified representation of an emulsion polymerization system.

Description of Process

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best described as proce
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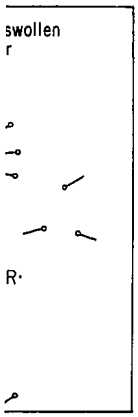

zation system.

The mechanism for *particle nucleation* (i.e., formation of polymer particles) is best described as proceeding by two simultaneous processes. One is the entry of radicals (either primary radicals or oligomeric radicals formed by solution polymerization) from the aqueous phase into the micelles (*micellar nucleation*). The other, *homogeneous nucleation* [16,17], involves solution-polymerized oligomeric radicals becoming insoluble and precipitating on themselves (or on dead oligomer). The precipitated species become stabilized by absorbing surfactant (from solution and the monomer droplets) and upon subsequent absorption of monomer are the equivalent of polymer particles formed by micellar nucleation. The relative extents of micellar and homogeneous nucleation would be expected to vary with the water solubility of the monomer and the surfactant concentration. Higher water solubility and low surfactant concentration favor homogeneous nucleation; micellar nucleation is favored by low water solubility and high surfactant concentration. (That homogeneous nucleation occurs is evidenced by the emulsion polymerization of systems where the surfactant concentration is below the CMC [18].) Homogeneous nucleation may be the primary mechanism of particle formation for a relatively water-soluble monomer such as vinyl acetate [19], while micellar nucleation is the predominant mechanism for a highly water-insoluble monomer such as styrene [20].

4-1b-3 Progress of Polymerization

A variety of behaviors are observed for the polymerization rate vs conversion depending on the relative rates of initiation, propagation and termination which are in turn dependent upon the monomer and reaction conditions (Fig. 4-2). Irrespective of the particular behavior observed, three *Intervals* (I, II, III) can be discerned in all emulsion polymerizations based on the *particle number N* (the concentration of polymer particles in units of number of particles per milliliter) and the existence of a separate monomer phase (i.e., monomer droplets). There is a separate monomer phase in Intervals I and II but not in III. The particle number increases with time in Interval I and then remains constant during Intervals II and III. Particle nucleation occurs in Interval I with the polymerization rate increasing with time as the particle number builds up. Monomer diffuses into the polymer particles to replace that which has reacted. The reaction system undergoes a very significant change during Interval I. The particle number stabilizes at some value which is only a small fraction, typically about 0.1%, of the concentration of micelles initially present. (N is in range 10^{13}-10^{15} particles per milliliter.) As the polymer particles grow in size and contain polymer as well as monomer, they absorb more and more surfactant (in order to maintain stability) from that which is in solution. The point is quickly reached at which the surfactant concentration in solution falls below its CMC, the inactive micelles become unstable and disappear with dissolution of micellar surfactant. By the end of Interval I or very early in Interval II all or almost all of the surfactant in the system has been absorbed by the polymer particles. As a consequence the monomer droplets are relatively unstable and will coalesce if agitation is stopped. Interval I is generally the shortest of the three intervals, its duration

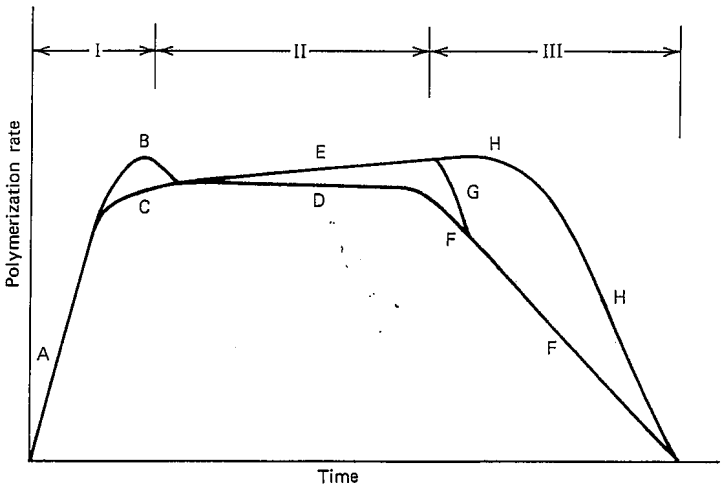

Fig. 4-2 Different rate behaviors observed in emulsion polymerization. After [5] (by permission of Wiley-Interscience, New York).

varying in the range 2–15% conversion. Interval I is longer for low initiation rates as more time is needed to attain the steady-state particle number. The more water-soluble monomers such as vinyl acetate tend to complete Interval I faster than the less water-soluble monomers. This is probably a consequence of the significant extent of homogeneous nucleation occurring simultaneously with micellar nucleation, resulting in achieving the steady-state particle number sooner. The predicted maximum in Fig. 4-2 (curve AC), arising from a transient high particle number and/or high proportion of particles containing propagating radicals, is often not distinguishable experimentally, since it is not a high maximum. The maximum is observed for many monomers when the initiation rates are sufficiently high.

Polymerization proceeds in the polymer particles as the monomer concentration in the particles is maintained at the equilibrium (saturation) level by diffusion of monomer from solution, which in turn is maintained at the saturation level by dissolution of monomer from the monomer droplets. The monomer concentration in the polymer particles is high; the volume fraction of monomer ϕ_m is 0.2, 0.3, 0.5, 0.6, 0.71, and 0.85 for ethylene, vinyl chloride, butadiene, styrene, methyl methacrylate, and vinyl acetate, respectively [5]. The polymerization rate either is constant (behavior D) or increases slightly with time (E) during Interval II. The latter behavior, which may begin immediately as shown in Fig. 4-2 or after a constant rate period, is a consequence of the gel or Trommsdorff effect (Sec. 3-10a). The polymer particles increase in size as the monomer droplets decrease. Interval II ends when the monomer droplets disappear. The transition from Interval II to III occurs at lower conversions as the water solubility of the monomer increases and the extent of swelling of the polymer particles by monomer increases [4,5]. For monomers (e.g., vinyl chloride) with low water solubility and low ϕ_m, the transition occurs at about 70–80% conversion. The transition occurs at progressively lower conversion as the proportion of the total monomer in the system that is con-

Quantitative Aspects

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$$r_p = k_p[\mathrm{M}]$$

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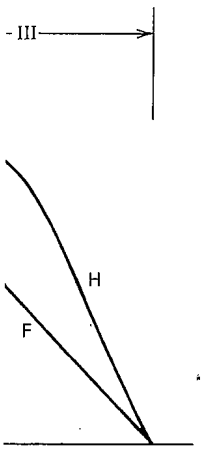

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r for low initiation rates as number. The more water- e Interval I faster than the ience of the significant ex- y with micellar nucleation, oner. The predicted maxi- gh particle number and/or ls, is often not distinguish- e maximum is observed for high.

ne monomer concentration tion) level by diffusion of the saturation level by dis- monomer concentration in nomer ϕ_m is 0.2, 0.3, 0.5, e, styrene, methyl methac- rization rate either is con- ring Interval II. The latter ig. 4-2 or after a constant ff effect (Sec. 3-10a). The plets decrease. Interval II ion from Interval II to III he monomer increases and omer increases [4,5]. For ty and low ϕ_m, the transi- on occurs at progressively r in the system that is con-

tained in the droplets decreases: styrene and butadiene at 40–50% conversion, methyl methacrylate at 25%, and vinyl acetate at 15% [19].

The particle number remains the same in Interval III as in Interval II but the monomer concentration decreases with time, since monomer droplets are no longer present. The decrease in ϕ_m is slower with the more water-soluble monomers as the monomer in solution acts as a reservoir. The presence of a gel effect continues in Interval III. The quantitative interplay of a decreasing monomer concentration with the gel effect determines the exact behavior observed in this interval (GF or H). Polymerization continues at a steadily decreasing rate as the monomer concentration in the polymer particles decreases. Final conversions of essentially 100% are usually achieved. The final polymer particles have diameters of the order of 500 to 2000 Å and are intermediate in size between the initial micelles and initial monomer droplets.

4-2 QUANTITATIVE ASPECTS

4-2a Rate of Polymerization

An expression for the rate of polymerization can be obtained by considering first the rate in a single polymer particle in which propagation is occurring (i.e., a particle containing a radical) and then the number of such particles. At the start of polymerization in a typical system where the concentration of micelles is 10^{18} per milliliter and the initiation rate is 10^{13} radicals per milliliter-second, a radical diffuses into a micelle every 10^5 sec at the start of Interval I. As the system progresses through Interval I, this time period decreases sharply, since the concentration of micelles is decreasing. A radical enters each particle on an average of every 10 sec during Intervals II and III where N is typically 10^{14} particles per milliliter. Once inside the micelle or polymer particle, a radical propagates in the usual manner at a rate r_p dependent on the propagation rate constant k_p and the monomer concentration [M] in the particle.

$$r_p = k_p[\mathrm{M}] \tag{4-1}$$

The monomer concentration is usually quite high since in many cases the equilibrium swelling of the particle by monomer is of the order 50–85% by volume. Values of [M] as high as 5 M are common.

Consider now what occurs on the entry of a radical into a particle which already has a radical. For most reaction systems, the radical concentration in a polymer particle is 10^{-6} M or higher. This is a higher radical concentration than in the homogeneous polymerization systems and the radical lifetime here is only a few thousandths of a second. The entry of a second radical into the polymer particle results in immediate bimolecular termination. Thus the polymer particle will have either one or zero radicals. The presence of two radicals in one particle is synonymous with zero radicals, since termination occurs so quickly. The particle is then dormant